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WADD TR 60-782, PT X

## VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

### PART X. THE DISSOCIATION ENERGY OF THE GROUP IV — GROUP VI MOLECULES

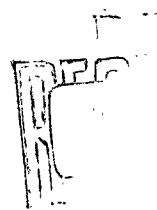
TECHNICAL REPORT NO. WADD-TR-60-782, PART X

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AERONAUTICAL SYSTEMS DIVISION  
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Project No. 7350, Task No. 735001

(Prepared under Contract No. AF61(052)-225  
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R. Colin and J. Drowart)



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## FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

# ABSTRACT

The available spectroscopic and thermochemical data for the dissociation energy of the group IV-group VI MeX molecules are reviewed and the best present values proposed. Correlations of several excited molecular states with atomic products are proposed.

This technical documentary report has been reviewed and is approved.



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## THE DISSOCIATION ENERGY OF THE GROUP IV-GROUP VI MOLECULES

Accurate convergence limits for one or more electronic states of most of the group IV (Me: C, Si, Ge, Sn, Pb)-group VI (X: O, S, Se, Te) molecules are known. This is in particular the case for CO<sup>(1)</sup>, a molecule not further discussed here and SiS, SiSe, GeS, SnO, SnS, SnSe and PbS, molecules for which the best known convergence limit is that of the excited E state. Accurate spectroscopic values  $D_0''$  for the dissociation energy of the ground state of these molecules can be derived therefrom, provided the correlation with atomic products is known. It has been postulated<sup>(2,3)</sup> that the E states of these molecules are analogous and correlate with the same atomic products. Recent rotational analysis for PbO<sup>(4)</sup> and SnO<sup>(5)</sup> showed that for the E state of these molecules, the most likely correlation is  $\text{Me}(^3P_1) + \text{O}(^3P_1)$ . Likewise the comparison of thermochemical and spectroscopic data for SnS and PbS<sup>(6)</sup> showed that their E state most probably correlates with  $\text{Me}(^3P_1) + \text{S}(^3P_{1,0})$ .

The purpose of this paper is to present a comparison between the spectroscopic data and recent thermochemical determinations of the dissociation energies of the group IV-group

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VI molecules, several of which were performed mass spectrometrically and to derive in each case the best present value for the dissociation energy. The comparison gives further support to the correlation of the E state with  $\text{Me}(^3\text{P}_1) + \text{X}(^3\text{P}_1)$ , which is then applied to all molecules of this group for which reliable data for this state are known. Other available spectroscopic data are also examined.

#### THERMOCHEMICAL DATA

The thermochemical data were in general obtained mass spectrometrically or from total pressure measurements supplemented with mass spectrometric analysis of the composition of the vapor. The mass spectrometric technique<sup>(7)</sup> and the instruments<sup>(8-10)</sup> used have been described previously.

The system studied, the temperature intervals covered and the composition of the vapor are summarized in Table I. This table shows that above MeX compounds, including SiO, GeO and SnO known to disproportionate to  $1/2 \text{MeO}_2(\text{s}) + 1/2 \text{Me}(\text{s}, \text{l})$ , the predominant molecule is MeX, polymers (and elements for GeTe, SnSe, SnTe, PbS, PbSe and PbTe) representing in general  $10^{-1}$  to  $10^{-4}$  in pressure, except for SnO and PbO, where  $(\text{SnO})_{1-4}$  and  $(\text{PbO})_{1-4}$  have comparable pressures. The  $\text{MeX}_2$  compounds vaporize mainly to  $\text{MeX}(\text{g}) + 1/2 \text{X}_2(\text{g})$ .  $\text{MeX}_2$  molecules were observed above  $\text{SiO}_2$ <sup>(11)</sup>,  $\text{SiS}_2$ , GeTe and SnTe.

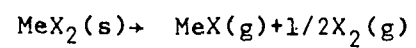
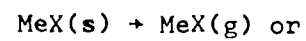
TABLE I: Gaseous Species in Equilibrium with Group IV-Group VI Compounds  
Standard Heats of Formation and of Sublimation

System	Composition of the vapour	Temperature range investigated (°K)	$-\Delta H_{298}^{\circ}$ , f Ref. kcal/mole	Ref.	$\Delta H_{298}^{\circ}$ , subl (b) kcal/mole	Ref.
$1/2 \text{ SiO}_2 + 1/2 \text{ Si}$	$\text{SiO}, \text{Si}_2\text{O}_2$	1200 - 1460	11	13	$85.5 \pm 1.5$	20
$\text{SiO}_2$	$\text{SiO}, \text{O}, \text{SiO}_2, \text{O}_2$	1750 - 1950	11	13	$198.5 \pm 1.5$	21
$\text{SiS}$	$\text{SiS}$	850 - 1140			$64.3 \pm 3.0$	
$\text{SiS}_2$	$\text{SiS}, \text{S}_2, \text{SiS}_2$	850 - 1140			$102.5 \pm 3.0$	
$\text{GeO}$	$(\text{GeO}, (\text{GeO})_2, (\text{GeO})_3)$	-			$50.6 \pm 2.5$	
$1/2 \text{ GeO}_2 + 1/2 \text{ Ge}$	$\text{GeO}, (\text{GeO})_2, (\text{GeO})_3$	750 - 950		14	$55.9 \pm 1.6$	
$\text{GeO}_2$	$\text{GeO}, \text{O}_2$	1020 - 1520		14	$(120.0 \pm 2.0)$	
$\omega$ $\text{GeS}$	$\text{GeS}$	-		15	$38.7 \pm 0.6$	22
$\text{GeTe}$	$\text{GeTe}, \text{Te}_2, \text{GeTe}_2$	870 - 954		16	$46.6 \pm 2.0$	23, 24
$1/2 \text{ SnO}_2 + 1/2 \text{ Sn}$	$\text{SnO}, (\text{SnO})_2, \text{O}_2$	1100 - 1400		16	$71.1 \pm 1.3$	
$\text{SnO}_2$	$\text{SnO}, \text{O}_2, (\text{SnO})_2$	1200 - 1500		16	$139.7 \pm 2.0$	
$\text{SnS}$	$\text{SnS}, (\text{SnS})_2$	835 - 1005	6	17	$52.6 \pm 1.6$	6
$\text{SnSe}$	$\text{SnSe}, (\text{SnSe})_2, \text{Se}_2$	790 - 1010			$51.1 \pm 2.0$	a, 25
$\text{SnTe}$	$\text{SnTe}, \text{Te}, \text{Te}_2, \text{SnTe}_2, (\text{SnTe})_2$	830 - 990		18	$52.5 \pm 1.6$	a, 25
$\text{PbO}$	$\text{PbO}, (\text{PbO})_2, \text{O}_2$	940 - 1180		19	$66.5 \pm 2.5$	
$\text{PbS}$	$\text{PbS}, (\text{PbS})_2, \text{Pb}, \text{S}_2$	865 - 1140	6	19	$55.7 \pm 1.6$	6
$\text{PbSe}$	$\text{PbSe}, \text{Pb}, \text{Se}_2$	1180 - 1450	12	18	$53.9 \pm 1.7$	26
$\text{PbTe}$	$\text{PbTe}, \text{Pb}, \text{Te}, \text{Te}_2$	923 - 1171	12	18	$53.8 \pm 2.0$	27

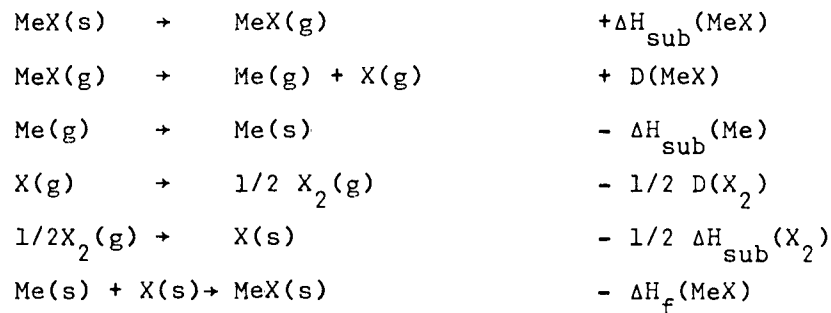
Legend of Table I:

a. this work

b.  $\Delta H^\circ_{298, \text{subl}}$  refers to the equilibrium



The dissociation energies  $D_0^0(\text{MeX})$  were calculated from thermochemical cycles of the type



Additional determinations based on the equilibrium

$\text{MeX(g)} \rightarrow \text{Me(s, l or g)} + 1/2 \text{X}_2(\text{g})$  were made for GeTe, SnSe, SnTe, PbS<sup>(6)</sup>, PbSe<sup>(12)</sup> and PbTe<sup>(12)</sup>.

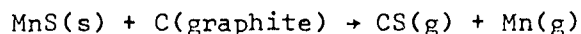
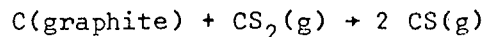
The heats of sublimation  $\Delta H_{\text{sub}}(\text{MeX})$  are summarized in Table II. The heats of sublimation of the group IV elements Me<sup>(28)</sup> and of the group VI molecules X<sub>2</sub><sup>(28)</sup> as well as the heats of formation of the compounds MeX or MeX<sub>2</sub> were in general taken from the literature. The values used for the dissociation energies  $D_{298}^0$  of O<sub>2</sub>, S<sub>2</sub>, Se<sub>2</sub>, and Te<sub>2</sub> were 119.10±0.05<sup>(28)</sup>, 102.0±2.0<sup>(29)</sup>, 75.4±2.0<sup>(30)</sup> and 52.5±2.0<sup>(12,31)</sup> kcal/mole respectively.

(It may be noted that the agreement between spectroscopic and thermochemical values of the dissociation energies of the group of molecules discussed in the following chapters is an indirect confirmation of the  $D_0^0(\text{S}_2)$ ,  $D_0^0(\text{Se}_2)$  and  $D_0^0(\text{Te}_2)$  values used).

For all the gaseous species Me,  $X_2$  and MeX, values for free energy function given in the literature<sup>(28,32)</sup> were used. For those stable compounds MeX and MeX<sub>2</sub> for which values are not given in the literature<sup>(32,33)</sup> estimates were made as follows. For solid SnTe, PbSe and PbTe<sup>(32)</sup>, the entropies at 298°K are known. For these compounds only the heat capacity, while for SiS, GeTe and SnSe both the entropy at 298°K and the heat capacity were estimated from the corresponding quantities for the elements using approximations discussed by Kubaschewski and Evans<sup>(18)</sup>. The corresponding quantities for GeS were derived from thermodynamic data for the reactions  $GeS(s) \rightarrow GeS(g)$ <sup>(22)</sup> and  $GeS(s) \rightarrow Ge(s) + 1/2 S_2$ <sup>(15)</sup>. The values obtained for the free energy functions are at 298°K, 12.0(SiS), 18.6(GeS), 20.3(GeSe), 22.2(GeTe), 22.5 (SnSe) and at 900°K 16.2(SiS), 23.0(GeS), 24.8(GeSe), 26.8 (GeTe), 28.0(SnSe), 29.8(SnTe), 30.0(PbSe) and 31.8(PbTe) cal/degree/mole.

The thermochemical data for each molecule are briefly discussed below

CS Thermochemical determinations<sup>(34)</sup> of the heat of formation of CS(g) were based on the reactions



Using the latter reaction for which the enthalpy change

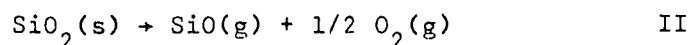
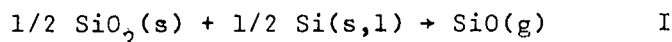
$\Delta H_{298}^0$  was measured to be  $178.5 \pm 0.5$  kcal/mole<sup>(34)</sup>,  $\Delta H_{298,f}^0(MnS(s)) = 49.5 \pm 0.5$  kcal/mole<sup>(35)</sup> and  $\Delta H_{298}^0(\text{sub Mn}) = 66.6 \pm 1.0$  kcal/

mole<sup>(28,30)</sup>, Freeman<sup>(37)</sup> calculated a value of 62.5 ±3.0 kcal/mole for the standard heat of formation of CS(g). This leads to a value  $D_0^{\circ}(\text{CS})=173.6\pm3.5$  kcal/mole (7.53±0.15 eV).

CSe Thermochemical data were obtained<sup>(38)</sup> for the reaction  $\text{C}(\text{graphite})+\text{Se}(\text{g}) \rightarrow \text{CSe}(\text{g})$   $\Delta H_0^{\circ}=-31.4\pm2.0$  kcal/mole whence  $D_0^{\circ}(\text{CSe})=138.4\pm2.5$  kcal/mole (6.00±0.10 eV)

CTe This molecule has hitherto not been observed. Its dissociation energy is estimated here as  $D_0^{\circ}=111\pm9$  kcal/mole (4.8±0.4 eV) by comparison with the other IV-VI molecules.

SiO The mass spectrometric data<sup>(11)</sup> confirm earlier conclusions that the main vaporization processes are

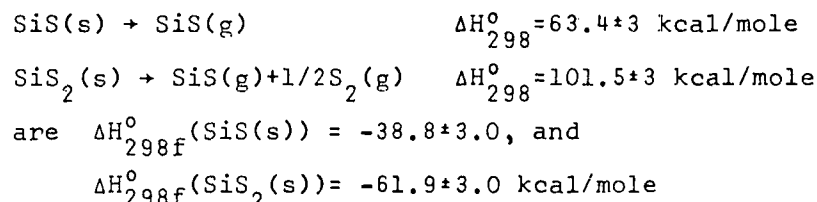


The heats of these reactions were taken as  $\Delta H_{298}^{\circ}=85.5\pm0.5$ <sup>(20)</sup> and  $\Delta H_{298}^{\circ}=198.3\pm1.5$ <sup>(21)</sup> kcal/mole respectively. To derive the heat of formation of SiO(g), the reaction<sup>(20)</sup>  $\text{SiO}_2(\text{s})+\text{H}_2(\text{g}) \rightarrow \text{SiO}(\text{g})+\text{H}_2\text{O}(\text{g})$  (III),  $\Delta H_{298}^{\circ}=134.8\pm2.0$  kcal/mole was further taken into account.

(For a more complete review, see Kubaschewski and Evans<sup>(18)</sup> and Schick<sup>(35)</sup>). The determination for reaction I and III are in good agreement with one another, while those for reaction II lead to slightly higher values. The recently redetermined standard heat of formation of  $\text{SiO}_2$ ,  $\Delta H_{298f}^{\circ}(\text{SiO}_2(\text{s}))=-217.7\pm0.2$  kcal/mole<sup>(13)</sup> was used

and the heat of sublimation of silicon taken as  $\Delta H_{298, \text{sub}}^{\circ}(\text{Si}) = 107.9 \pm 1.0$ , this being the average of several determinations<sup>(40)</sup>. The resulting mean value for the dissociation energy of  $\text{SiO}(\text{g})$  is  $D_0^{\circ}(\text{SiO}) = 191.9 \pm 3.0$  kcal/mole ( $8.32 \pm 0.13$  eV).

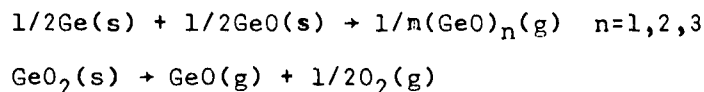
SiS No independent thermochemical data for this molecule were yet obtained. The spectroscopic value for the dissociation energy  $D_0'' = 6.38 \pm 0.06$  eV was used to calculate the heats of formation of  $\text{SiS}(\text{s})$  and  $\text{SiS}_2(\text{s})$  from mass spectrometric study of mixtures of  $\text{SiS}$  and  $\text{SiS}_2$  and from total pressure for  $\text{SiS}_2$ <sup>(41)</sup>. The heats of formation obtained in this manner from the reactions



The heat of formation of condensed  $\text{SiS}$  shows this compound not to be metastable up to about 1250°K, in agreement with observations by Retzlaff and Kohlmeyer<sup>(42)</sup>. The heat of formation of  $\text{SiS}_2$  is quite different from the discordant values given in the literature, which have anyway to be corrected for the recent values for the heat of formation of  $\text{SiO}$ <sup>(13)</sup>. The average value

selected by Kubaschewski and Evans<sup>(18)</sup>,  $61.6 \pm 6.0$  kcal/mole (corrected for  $\Delta H_f(\text{SiO}_2)$ ) is in agreement with the present value. The latter also makes it possible to explain the apparent boiling points of  $\text{SiS}_2$  at about  $1400^\circ\text{K}$  as being that of the  $\text{Si} + \text{SiS}_2$  system.

GeO Earlier thermochemical values were based on vapor pressure determination for  $\text{GeO}$ <sup>(43)</sup> and  $\text{Ge} + \text{GeO}_2$ <sup>(14,43)</sup>. The evaporation behavior of  $\text{Ge} + \text{GeO}_2$  and  $\text{GeO}_2$  were examined mass spectrometrically. The evaporation processes are



The mass spectrometric results for  $\text{GeO}_2$  obtained here are in disagreement with an earlier investigation<sup>(44)</sup>, also by mass spectrometry, which seems to be characteristic of  $\text{Ge} + \text{GeO}_2$  rather than of  $\text{GeO}$ . The enthalpy for the reaction

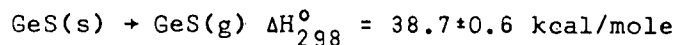
$1/2\text{GeO}_2(\text{s}) + 1/2\text{Ge(s)} \rightarrow \text{GeO(g)}$   $\Delta H_{298}^\circ = 55.9 \pm 1.6$  kcal/mole was calculated from mass spectrometric pressure measurements made independently, as well as from the total pressures given in the literature<sup>(14,43)</sup> correcting these for the presence of  $(\text{GeO})_2$  and  $(\text{GeO})_3$ . A similar procedure was adopted for  $\text{GeO(s)}$ , for which a heat of formation  $\Delta H_{298}^\circ = -58.9 \pm 3.0$  kcal/mole was



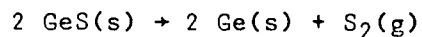
derived from the earlier data<sup>(43)</sup> in satisfactory agreement with direct determinations<sup>(45)</sup>. The best average of all data gives  $D_0^0(\text{GeO}) = 156.6 \pm 3.0$  kcal/mole ( $6.79 \pm 0.13$  eV). The enthalpy of the reaction  $\text{GeO}_2(\text{s}) \rightarrow \text{GeO}(\text{g}) + 1/2 \text{O}_2(\text{g})$  was not measured. As a result of interaction with  $\text{SiO}_2$  crucible the pressures in the literature<sup>(46)</sup> are low. The enthalpy given in Table I was calculated from the heat of formation of  $\text{GeO}_2(\text{s})$  and the above dissociation energy of  $\text{GeO}(\text{g})$ .

GeS The mass spectrometric analysis of the vapor showed only the monomer GeS in the gas phase.

The enthalpy of the reaction



is hence very well known from a number of pressures measurements<sup>(22)</sup> which are all in very good agreement except that of Kenworthy and coworkers which seems to be a factor of approximately 3 too high. The heat of formation of GeS was evaluated from the reaction<sup>(15)</sup>



and yields

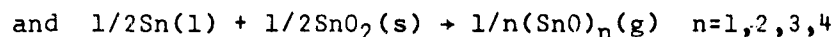
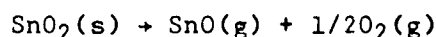
$$\Delta H_{298f}^0(\text{GeS}) = -16.2 \pm 1.3 \text{ kcal/mole}$$

Inserting these values in the cycle given above, one obtains  $D_0^0(\text{GeS}) = 133.3 \pm 3.5$  kcal/mole ( $5.78 \pm 0.15$  eV).

GeSe The total vapor pressure above GeSe was measured by Liu Ch'Un-Hua, Pashinkin and Novoselova<sup>(24)</sup>. Using the spectroscopic value of the dissociation energy  $D_0^{\circ}(\text{GeSe}) = 113.1 \pm 0.7$  kcal/mole discussed below, it can be shown that the decomposition pressure of  $\text{Se}_2$  is low compared to that of the main species  $\text{GeSe(g)}$ . The total pressure measurements yield therefore a value of the heat of sublimation  $\Delta H_{298\text{sub}}^{\circ}(\text{GeSe}) = 44.6 \pm 1.5$  kcal/mole obtained by 2nd (44.2) and 3rd law (44.8) procedures. Combining this value with  $D_0^{\circ}(\text{GeSe})$ , a heat of formation  $\Delta H_{298\text{f}}^{\circ}(\text{GeSe(s)}) = -14.4 \pm 3.0$  kcal/mole is obtained.

GeTe The mass spectrometric investigation of the decomposition of the vapor showed the presence of  $\text{GeTe}$ ,  $\text{Te}_2$ ,  $(\text{GeTe})_2$  and  $\text{GeTe}_2$ . The pressure of the  $\text{Te}_2$  molecule, relative to that of the main species  $\text{GeTe(g)}$  is  $10^{-1}$  at  $880^{\circ}\text{K}$ . Using total vapor pressure measurements<sup>(23,24)</sup> to evaluate the partial pressures, a heat of sublimation  $\Delta H_{298,\text{sub}}^{\circ}(\text{GeTe}) = 46.6 \pm 2.0$  kcal/mole and a heat of formation  $\Delta H_{298\text{f}}^{\circ}(\text{GeTe(s)}) = -4.2 \pm 2.0$  kcal/mole were calculated from 3rd law procedures (2nd law:  $\Delta H_{298\text{sub}}^{\circ}(\text{GeTe}) = 47.8^{(23)}, 46.7^{(24)}$ ). These values lead to the dissociation energy  $D_0^{\circ}(\text{GeTe}) = 92.4 \pm 3.0$  kcal/mole ( $4.00 \pm 0.13$  V.)

SnO The heats of both reactions



were studied mass spectrometrically. The values obtained are  $\Delta H_{298}^{\circ} = 139.7 \pm 2.0$  and  $71.1 \pm 1.3$  kcal/mole (for  $n=1$ ) respectively. Whence  $D_0^{\circ}(\text{SnO}) = 127.2 \pm 2.0$  kcal/mole ( $5.53 \pm 0.10$  eV).

Total pressure determinations were examined for comparison. The vapor pressure measurements of  $\text{SnO}_2(\text{s})$  by the Knudsen method<sup>(47)</sup> were not included, since the sample interacted with the crucible material<sup>(16)</sup>  $\text{SiO}_2$ . The pressure determination by the transport method<sup>(16)</sup> gives too high values because the polymers  $(\text{SnO})_{2-4}$  contribute to the weight loss. Estimating their contribution from the mass spectrometer data yields  $D_0^{\circ} = 130.5 \pm 3.0$  kcal/mole ( $5.64 \pm 0.13$  eV) in agreement with the direct determinations.

SnS The thermochemical value for the dissociation energy based on mass spectrometry and vapor pressure data is  $D_0^{\circ}(\text{SnS}) = 110.1 \pm 3.0$  kcal/mole ( $4.78 \pm 0.13$  eV). For a detailed discussion see reference (6).

SnSe The composition of the vapor as well as partial pressures were determined mass spectrometrically. The pressure of the main component, SnSe, was found in good agreement with pressure determinations by the effusion method<sup>(25)</sup>. These data lead to a value for the heat of sublimation:  $\Delta H_{298, \text{sub}}^{\circ}(\text{SnSe}) = 51.1 \pm 2.0$  kcal/mole (3rd law). From the partial  $\text{Se}_2$  pressure, a heat of formation  $\Delta H_{298f}^{\circ}(\text{SnSe}) = -19.9 \pm 1.5$  kcal/mole was derived compared to the estimated value  $-16.5 \pm 2$  kcal/mole<sup>(18)</sup>. These values lead to  $D_0^{\circ}(\text{SnSe}) = 94.8 \pm 4.0$  kcal/mole ( $4.11 \pm 0.17$  eV).

SnTe The composition of the vapor and partial pressures were determined as above. The SnTe pressure was again in good agreement with total pressure measurements by the effusion method<sup>(25)</sup>. The  $\text{Te}_2$  partial pressure gave a value of  $-14.7 \pm 2.0$  for the heat of formation of SnTe(s), in good agreement with  $\Delta H_{298f}^{\circ} = -14.6 \pm 0.3$  kcal/mole<sup>(18)</sup>, thereby confirming the values of the free energy function of SnTe(s) used. The 2nd and 3rd law values, 47.5 and 52.3 kcal/mole respectively, for the heat of sublimation are in less good agreement. Preference is given to the 3rd law value, which leads to  $D_0^{\circ}(\text{SnTe}) = 79.8 \pm 3.0$  kcal/mole ( $3.46 \pm 0.17$  eV).

PbO The mass spectrometric analysis of the vapor above PbO(s) showed the presence of  $(\text{PbO})_{1-4}$ . The enthalpy change for the reaction



was calculated as being  $\Delta H_{298} = 65.8 \pm 1.5$  kcal/mole from total pressure measurement given in the literature<sup>(48)</sup> taking the composition of the vapor into account. This value combined with the heat of formation of PbO(s),  $\Delta H_{298f} = -52.4 \pm 0.2$  kcal/mole<sup>(19)</sup> leads to  $D_o^0(\text{PbO}) = 92.2 \pm 3.0$  kcal/mole (4.00  $\pm$  0.13 eV).

PbS Mass spectrometric<sup>(6)</sup> and vapor pressure data combined with  $\Delta H_{298f} = 22.5 \pm 0.5$  kcal/mole<sup>(18)</sup> lead to  $D_o^0(\text{PbS}) = 78.9 \pm 0.25$  kcal/mole (3.42  $\pm$  0.12 eV). For a detailed discussion see reference (6).

PbSe The knowledge of the dissociation energy of this molecule is not satisfactory. The mass spectrometric investigation of the vapor by Porter<sup>(12)</sup> shows PbSe to be the main gaseous species. Hence one calculates from the published pressure measurements<sup>(24)</sup> a heat of sublimation of 53.9 kcal/mole (2nd law: 53.2), which combined with the estimated heat of formation  $\Delta H_{298f}^0(\text{PbSe}) = -18.0 \pm 2.0$  kcal/mole<sup>(18)</sup> gives  $D_o^0(\text{PbSe}) = 65.0$  kcal/mole (2.82 eV). Direct measurements made in double oven type Knudsen cells by Porter<sup>(12)</sup> give

for the reaction  $\text{PbSe(g)} \rightarrow \text{Pb(g)} + \text{Se(g)}$  values ranging from 60.0 to 64.5 kcal/mole, with an average of 62.9 kcal/mole. Simultaneous measurements for the reaction  $\text{Pb(g)} + \text{Se}_2\text{(g)} \rightarrow \text{PbSe(g)} + \text{Se(g)}$  give however  $\Delta H_{298}^{\circ} = 2.7 \pm 1.0$  kcal/mole, which combined with  $D_{298}^{\circ}(\text{Se}_2) = 75.4 \pm 2.0$  kcal/mole<sup>(30)</sup> would give  $D_{298}^{\circ}(\text{PbSe}) = 72.7 \pm 3.0$  kcal/mole ( $D_0^{\circ} = 72.0 \pm 3.0$ ). Until a direct determination of the heat of formation of  $\text{PbSe(s)}$  is available, an average value  $D_0^{\circ}(\text{PbSe}) = 63 \pm 5$  kcal/mole ( $2.95 \pm 0.22$  eV) is selected.

PbTe The dissociation energy of  $\text{PbTe}$  was measured mass spectrometrically by Porter<sup>(12)</sup>, who obtained  $D_0^{\circ}(\text{PbTe}) = 51.4 \pm 2.0$  kcal/mole. This figure is in agreement with the value  $D_0^{\circ}(\text{PbTe}) = 55.0 \pm 2.0$  kcal/mole (2nd law: 52.9) that can be derived from the vapor pressure measurements<sup>(25)</sup> (main component  $\text{PbTe}$ ) and the heat of formation of  $\text{PbTe(s)}$ ,  $\Delta H_{298f}^{\circ} = -16.6 \pm 0.5$  kcal/mole<sup>(19)</sup>. The average value  $D_0^{\circ}(\text{PbTe}) = 53.1 \pm 3.0$  kcal/mole ( $2.30 \pm 0.17$  eV) is selected.

The thermochemical values  $D_0^{\circ}$  for the dissociation energies of the group IV-group VI molecules have been assembled in Table V.

## SPECTROSCOPIC DATA

The spectroscopic data considered in the present paper have been collected in table II and were all taken from the literature. Only the following comments seem necessary for the purposes of this paper. For the molecules SiS, GeS, GeSe, GeTe, SnO and SnSe graphical extrapolations for the E state could be made. For GeS, GeSe, SnO, SnS, SnTe and PbS, the extrapolation were confirmed or supplemented by direct observation of convergence limits (continua) for the same or other states. For GeTe, PbO and possibly PbSe the value given for the convergence limit of the E state corresponds to the wavelength down to which vibrational structure lines could be observed. For the molecule GeTe the value of the convergence limit is somewhat uncertain, since it was estimated by analogy with GeS and GeSe. It should however not be lower than 4.38 eV, since the vibrational levels are known up to that energy. For the molecule SiTe, for which the linear Birge Sponer limit for the E state was not calculated because of the presence of large anharmonic and cubic terms, the extrapolation was nevertheless made here to serve as a guide for obtaining a spectroscopic value for the dissociation energy, since no other data are available.





TABLE II. (Continued)

Molecule	State	$\nu_{00}$ cm <sup>-1</sup>	$\omega$ cm <sup>-1</sup>	$x\omega$ cm <sup>-1</sup>	$y\omega$ cm <sup>-1</sup>	$\omega^2/4x\omega$ ev	Convergence Limit		Ref.
							linear ev	graph. observ. ev	
GeSe	X	0	408.7	1.36		3.80	3.80		
	D	30776.0	269.4	0.89		2.53	6.35		
	E	35367.1	217.7	1.02		1.44	5.83	5.23	5.25
GeTe	X	0	323.9	0.25		5.98	5.98		54
	D	27699.3	221.0	0.89		1.71	5.15		
	E (31393)	170		(1.2)		0.77	(4.67)	4.49	>4.38
SnO	X	0	822.4	3.73		5.62	5.62		3
	B (25325)	(575)							
	D	29505.1	582.8	3.08		3.42	7.08	(5.04) <sup>b</sup>	
	E	36138	508.0	2.9		2.76	7.23	5.68	6.40-6.44
	o	~51775							
	P	57491							
	F	58752	724	21		0.77	8.05		
	X	0	485.9	1.358		5.39	5.39		55
	D	28180.8	330.08	1.265		2.51	6.01		
SnS	E	32939.6	295.05	1.09	-0.012	2.49	6.58	5.06	56
	P	52174.5	(395)						
	q	55928							~6.96
SnSe	r	56470-890						~7.05	
	X	0	331.2	0.736		4.63	4.63		57,58
	A	19299.3	223.2	0.88		1.76	4.15		
	B	21795	(220)						
	C	22695	(220)						
	D	27496.6	225.1	0.69		2.28	5.69		
	E	30671.6	196.6	0.77	-0.0016	1.56	5.36	4.54	
	F	(47830)	(290)						

TABLE II. (Continued)

Molecule	State	$\nu_{\text{OQ}}$ cm <sup>-1</sup>	$\omega$ cm <sup>-1</sup>	$x\omega$ cm <sup>-1</sup>	$y\omega$ cm <sup>-1</sup>	$\omega^2/4x\omega$ ev	Convergence Limit		Ref.
							linear ev	graph. observ. ev	
SnTe	X	O	259.5	0.50		4.18	4.18		57,58
	A	16803.5	178.5	0.44		2.25	4.33		
	B	20380.0	230.3	1.53	-0.013	1.08	3.61	(3.34) <sup>b</sup>	
	C	21397.8	218.1	0.98		1.51	4.17		
	D	25404.1	179.1	0.40		2.48	5.63		
	E	27580.2	135.0	2.5		0.22	3.64	(4.07)	
	G	28465.0	98.0	1.0		0.30	3.83		
	H	29042.5	200.8	0.3		4.17	7.82		
	I	30789.0	201.0	0.6	-0.003	2.09	5.91	6.56	
	F	44018.4	229.7	1.25		1.32	6.78		
	J	(47245)	(230)						
PbO	X	O	721.8	3.70		4.37	4.37		4
	A	20088	451.7	3.33		1.89	4.38		
	a								
	B	22531	493.5	2.26		3.33	6.02		
	C	24108	(534)	(3.9)		(2.27)	(5.26)		
	C'	25720	(475)						
PbS	D	30484	(530.5)	(2.92)		(2.99)	(6.77)	>4.86	59
	E	34680	(440)						
	X	O	428.14	1.201		4.74	4.74		60
	A	18768.0	261.09	0.365		5.80	8.13		
	B	21774.8	282.17	0.856		2.89	5.59		
	C	23150.7	303.93	1.436		2.00	4.87		
	C'	24952.3	283.95	1.171		2.14	5.24		
	D	29586.0	299.34	1.574		1.77	5.44		
	E							4.55	59
	F	47739		(7.8)					

TABLE II. (Continued)

Molecule	State	$\nu_{00}$ cm <sup>-1</sup>	$\omega$ -1 cm	$x\omega$ -1 cm	$y\omega$ -1 cm	$\omega^2/4x\omega$ ev	Convergence Limit			Ref.
							linear	graph	observ.	
							ev	ev	ev	
PbSe	X	0	277.6	0.51		4.69	4.69			59,61
	A	18661.5	166.9	0.14		6.03	8.35			
	B	20959.4	184.8	0.43		2.46	5.06			
	C	23268.5	183.0	0.25		4.15	7.04			
	D	28374.4	190.4	0.53	-0.004	2.12	5.64	(4.75) <sup>b</sup>		
	E								4.32	
PbTe	F	45194.5	224.8	0.50		3.13	8.73			
	X	0	211.96	0.43		3.17	0.17			59,62
	A	18363.05	127.08	0.105		4.77	7.05			
	B	19704.30	144.89	0.446		1.46	3.90			
	D	27141.8	142.6	1.58		0.40	3.76			
	F	41641.0	176.4	1.0		0.92	6.09			
	G	46515.5	159.6	1.4		0.60	6.37			

- a. In most cases the letter label is that of the ref. quoted; it may be different from that used in ref.58.
- b. Numerically calculated using the formula  $E = \omega\nu + x\omega\nu^2 + y\omega\nu^3$ .

## COMPARISON OF THERMOCHEMICAL AND SPECTROSCOPIC DATA.

This comparison will be started with the E state, since this is the only state for which in general accurate values for the convergence limit are available.

It had already been concluded, on the basis of the agreement between the convergence limits for this state and the Birge Spomer value for the dissociation energy of the ground state, that this state correlates with  $\text{Me}(^3\text{P}) + \text{X}(^3\text{P})^{(3)}$ .

Inspection of the multiplet splittings given in Table III, shows that, in order to decide on the basis of a comparison of spectroscopic and thermochemical data, which  $\text{Me}(^3\text{P}_{0,1,2})$  and  $\text{X}(^3\text{P}_{2,1,0})$  sublevel are involved the more favorable cases would be CSe, CTe, SiSe, SiTe and perhaps GeSe and GeTe for  $\text{X}(^3\text{P})$  and SnO, SnS, PbO and PbS for  $\text{Me}(^3\text{P})$ . Unfortunately, the available data preclude such comparison for CSe, CTe, SiSe, SiTe and GeSe. This comparison can however be made for GeTe, SnO, SnS, PbO, PbS and also SnSe, SnTe and to a certain extent PbSe.

It has already been shown for SnS and PbS that such a comparison leads to the conclusion that the E state correlates with  $\text{Me}(^3\text{P}_1) + \text{X}(^3\text{P}_{1,0})^{(6)}$ .

TABLE III. Excitation energy of  $^3P_{0,1,2}$  and  $^1D_2$  states of the elements of Group IV and VI(in ev).

	$^3P_0$	$^3P_0$	$^3P_2$	$^1D_2$
C	0	0.002	0.005	1.27
Si	0	0.01	0.03	0.78
Ge	0	0.07	0.18	0.89
Sn	0	0.21	0.43	1.07
Pb	0	0.97	1.32	2.68
O	0.03	0.02	0	1.97
S	0.07	0.05	0	1.15
Se	0.31	0.25	0	1.19
Te	0.58	0.58	0	1.31

This conclusion is confirmed by a similar comparison for the molecules SnO, SnSe and PbO and to a certain extent GeTe, SnTe and PbSe, as shown in Table IV. The only molecule for which there seems to be a discrepancy between the dissociation energy so derived from the spectroscopic data of the E state and the thermochemical value is SnTe. It may however be noted that the spectroscopic data for the E state of all tellurides are not satisfactory. For SnTe only a region of apparently continuous absorption is known and interpreted as a possible convergence limit of the E state leading to the value 4.07 e.V. which according to the authors<sup>(57)</sup> "should be treated with considerable reserve".

The accuracy of the thermochemical data makes it difficult to distinguish between the  $X(^3P_1)$  and  $X(^3P_1)$  sublevels, the separation of which is maximum 0.06 e.V. for  $X = \text{Se}$ . From the rotational analysis of several states of the molecule PbO, Barrow, Deutsch and Travis<sup>(4)</sup> have concluded on the basis of the  $\Omega$  correlation rule and the non-crossing rule, that the most likely correlations for several  $O^+$  states of this molecule are as indicated in Table IV. Professor Barrow has kindly informed us that a similar analysis for SnO also gives as most likely correlation for the E state,  $\text{Sn}(^3P_1) + O(^3P_1)$ .

The interpretation of the rotational analysis and the comparison of the thermochemical and spectroscopic data are thus in agreement and in fact confirm and supplement one another.

The conclusion that the E state of the group IV-group VI molecules correlate with  $\text{Me}(^3P_1) + \text{X}(^3P_1)$  has therefore been extended in Table V to the molecules SiS, SiSe, SiTe, GeS and GeSe for which accurate convergence limits of the E state and no thermochemical data are available. The dissociation energies of SiS and GeSe so obtained were already used in the section dealing with thermochemical data to derive the heats of formation of the corresponding compounds.

If the correlation of the E state thus seems established it is less easy to derive the correlations of the other states. The fact that most combinations of  $\text{Me}(^3P_1) + \text{X}(^3P_1)$  sublevels can lead to one or several  $\Omega = 1$  molecular states make it difficult to propose off hand a correlation for the B(1) and D(1) states. The convergence limit of the B state for SnTe, 3.34 e.V., calculated from the formula  $E = \omega v + x\omega v^2 + y\omega v^3$  with  $\omega = 230.3$ ,  $x\omega = 1.53$ ,  $y\omega = -0.013\text{cm}^{-1}$  would indicate that this state correlates with  $\text{Sn}(^3P_0) + \text{Te}(^3P_2)$ . The B state in PbTe, known up to 2.65 e.V. can however not correlate with  $\text{Pb}(^3P_0) + \text{Te}(^3P_2)$  at  $2.23 \pm 0.10$  e.V. and should at least correlate with  $\text{Pb}(^3P_0) + \text{Te}(^3P_1)$  or any combination

$\text{Pb}(^3\text{P}_1) + \text{Te}(^3\text{P}_{2,1,0})$ . If the convergence limit of  $\text{SnTe}$  is considered to be low, but not off by more than 0.5 e.V; and if the B states of both molecules is analogous as would be indicated by the same ratio  $\omega_B/\omega_X$ , then the probable correlation of the B state would be  $\text{Me}(^3\text{P}_0) + \text{X}(^3\text{P}_1)$ . (Table IV).

TABLE IV. Correlation of the X, A, B, C, D and E States  
of the Group IV-Group VI MeX molecules.

Atomic States Me	X	Possible $\Omega$ values	likely mole cular states
$^3\text{P}_0$	$^3\text{P}_2$	$0^+$ , 1, 2	$\text{X}(0^+)$
	$^3\text{P}_1$	$0^-$ , 1	$\text{B}(1)?$
	$^3\text{P}_0$	$0^+$	$\text{A}(0^+)$
$^3\text{P}_1$	$^3\text{P}_2$	$0^-(2)$ , $0^+$ , 1(3), 2(2), 3	$\text{C}(0^+)$
	$^3\text{P}_1$	$0^-$ , $0^+(2)$ , 1(2), 2	$\text{E}(0^+)$
	$^3\text{P}_0$	$0^-$ , 1	$\text{D}(1)?$
$^3\text{P}_2$	$^3\text{P}_2$	$0^-(2)$ , $0^+(3)$ , 1(4), 2(3), 3(2), 4	
	$^3\text{P}_1$	$0^-(2)$ , $0^+$ , 1(3), 2(2), 3	
	$^3\text{P}_0$	$0^+$ , 1, 2	

It is even less easy to speculate about the correlation of the D state. In  $\text{PbTe}$ , the difference between the convergence limit of this D state,  $3.67 \pm 0.20$  e.V. obtained from a linear Birge Sponer extrapolation and the thermoche-



mical value for the dissociation energy  $D_0^0 = 2.30 \pm 0.17$  is  $1.37 \pm 0.37$  e.V. It may be noted that the uncertainty quoted on the Birge Sponer extrapolation corresponds to an uncertainty as high as  $\pm 70\%$ , which still would not affect the conclusion since the linear dissociation energy of the D state itself is only 0.4 e.V. This difference compared to the excitation energies of the different  $^3P_{0,1,2} + ^3P_{2,1,0}$  combinations for Pb and Te, 0, 0.58, 0.58, 0.97, 1.55, 1.55, 1.32, 1.90 and 1.90 e.V., indicates that possible correlations are  $Pb(^3P_1) + Te(^3P_{1,0})$  or  $Pb(^3P_2) + Te(^3P_2)$ . A selection between those two correlations cannot be made on the basis of the highest vibrational level of the D state observed in any of the MeX molecules. A possible argument for the  $^3P_1 + ^3P_{1,0}$  correlation could be that the linearly extrapolated convergence limit of the D state lies either above or below the similarly evaluated limit of the E state when the excitation energy  $Me(^3P_1) + X(^3P_{1,0})$  is either larger or smaller than  $Me(^3P_2) + X(^3P_2)$  for 8 (SiSe, SiTe, GeSe, GeTe, SnO, SnS, SnSe, SnTe) out of 12 molecules of which two (GeO, GeS) have both limits essentially at the same level and two (SiO, SiS) present the inverse situation.

The F states, have already been shown<sup>(3)</sup> to correlate with  $Me(^1D_2) + X(^1D_2)$ . They have not been observed for all molecules of this group and will not be discussed here. For SnSe the combination  $Sn(^1D_2) + S(^1D_2)$  leads to

one shallow and one repulsive state, from which accurate values of the dissociation energy can be derived (see footnote c, Table V).

For SnTe, higher molecular states G, H and I are known. Perhaps could these states be correlated with  $\text{Sn}(^3\text{P}_2) + \text{Te}(^3\text{P}_{2,1,0})$ . The term values  $\nu_{\infty}$  increase regularly for the A to I states and an abrupt increment for the F state. The same situation occurs for the other molecules of this group as can be seen from Table II.

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TABLE V. Comparison of spectroscopic  $D_0''$  and thermochemical  $D_0^0$  value of the dissociation energies of group IV-group VI molecules (in e.v.)

Molecule	Convergence limit E state	Excitation energy Me( $^3P_1$ )+X( $^3P_1$ )	$D_0''$	$D_0^0$
CO			11.111±0.06	
CS				7.53±0.15
CSe				6.00±0.15
CTe				(4.8 ±0.4)(a)
SiO				8.32±0.15
SiS	6.44±0.06	0.06	6.38±0.06	
SiSe	5.66±0.15	0.26	5.40±0.15	
SiTe	(4.70±0.25)	0.59	(4.11±0.25)	
GeO				6.79±0.13
GeS	5.79±0.03	0.12	5.67±0.03	5.78±0.15
GeSe	5.25±0.08	0.32	4.93±0.03	
GeTe	4.49 +0.30 -0.10	0.65	3.84 +0.30 -0.10	4.00±0.15
SnO	5.68±0.05	0.23	5.45±0.05 5.37(b)	5.53±0.13
SnS	5.06±0.10	0.26	4.80±0.10 4.74(c) 4.83(c)	4.78±0.12
SnSe	4.54±0.06	0.46	4.08±0.06	4.11±0.17
SnTe	(4.07)?	0.79	(3.28)?	3.45±0.17
PbO	≥4.86	0.99	≥ 3.87	4.00±0.13
PbS	4.55±0.20	1.02	3.53±0.20	3.42±0.12
PbSe	≥4.32 ?	1.22	≥ 3.10?	2.95±0.22
PbTe				2.30±0.17

a estimated

b from absorption continuum at 1926 to 1937 Å, correlated<sup>(3)</sup> with Sn( $^1D_2$ )+O( $^3P$ ). It was assumed here that the O( $^3P_2$ ) sub-level is involved. If the absorption occurred from  $v''=1$ , which could be the case as a result of the large interatomic equilibrium distance in the shallow upper state, the value obtained  $D_0''=5.47$  eV would be in perfect agreement with  $D_0''=5.45$  eV.

c from shallow q and repulsive r state respectively, assuming both to correlate with Sn( $^1D_2$ ) + S( $^1D_2$ )

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<p>Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio. Rpt Nr WADD-TR-60-782, Pt X. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: The Dissociation Energy of the Group IV-Group VI Molecules. Final report, May 63, 32p. incl tables, 62 refs.</p> <p>Unclassified Report</p> <p>The available spectroscopic and thermochemical data for the dissociation energy of the group IV-group VI MeX molecules are reviewed and the best present values proposed. Correlations of several excited molecular states with atomic products are proposed</p>	<p>1. Thermochemical and spectroscopic data</p> <p>2. Dissociation energies of molecules</p> <p>I. AFSC Project 7350, Task 735001</p> <p>II. Contract AF 61</p> <p>III. Universite Libre de Bruxelles, Brussels, Belgium</p> <p>IV. R. Collin, J. Drowart</p> <p>V. Aval fr OHS</p> <p>VI. In ASTIA collection</p>		
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